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Indium and Thallium Extraction into Betainium *Bis*(trifluoromethylsulfonyl)imide Ionic Liquid from Aqueous Hydrochloric Acid Media

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Abstract

The partitioning behavior of indium and thallium ions between aqueous hydrochloric acid solutions and hydrophobic betainium *bis*(trifluoromethylsulfonyl)imide ionic liquid was studied using a standard liquid-liquid extraction technique. The experiments were mainly carried out by means of a radiochemical method, using ^{111}In and ^{201}Tl medical radionuclides at an ultra-trace concentration. Both mono- and trivalent thallium were utilized and the highest oxidation state (3+) was produced by adding either chlorine or bromine water to the aqueous phase prior to extraction. The metal ion transfer was optimized by varying the aqueous concentration of hydrochloric acid and by introducing zwitterionic betaine as an extracting agent into the aqueous phase. It was found that the highest *D* values of In(III), Tl(III) and Tl(I) in the investigated chemical systems were up to 200, 70, and 1, respectively. The influence of the addition of lithium salt, having common with the ionic liquid counterion, and the variation of mixing time on the distribution ratio of the metal ions were also studied. To understand the underlying extraction mechanism of the metal ions and to propose the predominant extracted species, mathematical models based on ion pair formation and ion exchange were developed.

Keywords: Indium, thallium, ionic liquid, betainium *bis*(trifluoromethylsulfonyl)imide, zwitterion, liquid-liquid extraction.

1. Introduction

Ionic liquids (ILs) are salts composed of discrete cations and anions which have a melting temperature below 100° C. [1-3] These compounds have been used in various research fields such as organic synthesis, [4-7] catalysis [8-12] and electrocatalysis, [13] electrochemistry, [14] nanoparticle formation, [15] and solvent extraction. [16-18] Specifically for solvent extraction, the hydrophobic room-temperature ILs have been widely considered as an alternative to conventional molecular solvents due to their wide liquid range, negligible vapor pressure, low toxicity, low flammability, and ability to solubilize various solutes. [19]

The availability of various cationic and anionic combinations results in a large diversity of structures and properties of the ILs. [20] Among those, we are interested in a specific type of ionic liquids, which are simultaneously hydrophobic and protic. For example, such an ionic liquid is betainium *bis*(trifluoromethylsulfonyl)imide (denoted as [Hbet][Tf_2N]). This IL has a functionalized carboxylic group in its cationic part which has the ability to coordinate with metal ions. [21] The building block of the IL cation is glycine betaine, which is a zwitterion and is hydrophilic in nature. Its combination with the hydrophobic anion *bis*(trifluoromethylsulfonyl)imide results in an ionic liquid that forms a biphasic system with water at room temperature. Since it is hydrophobic and liquid at room temperature, this IL can be used as an "all-in-one" solvent, *i.e.*, it could play the role of both metal extracting agent and diluent in the extraction system. Additionally, it has been shown that [Hbet][Tf_2N] can be reused after its first extraction cycle, [22, 23] which makes it appealing for efficient use of solvents. The chemical structure of [Hbet][Tf_2N] is shown in Fig. 1.

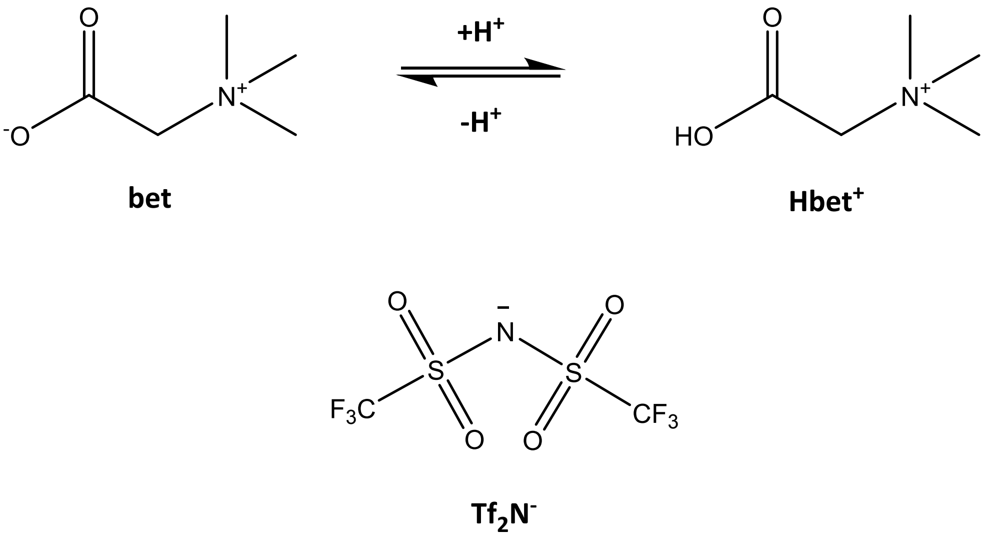

Fig. 1. Chemical structure of the ions constituting the [Hbet][Tf_2N] ionic liquid studied in this work: zwitterionic betaine and betainium cation (top) and *bis*(trifuoromethanesulfonyl)imide anion (bottom).

The first [Hbet][Tf_2N] implementation was aimed at selective dissolution of metal oxides. [21] Since then, this IL has been applied to metal extraction and separation from various media. For example, it was used to extract trivalent rare-earth elements, [24] scandium, [23] actinides, [25] indium and gallium (from water). [24] It was also used as the organic phase media for the partition of platinum group metals such as ruthenium(III), rhodium(III), and palladium(II) [26-28] and uranyl species from nitric acid media. [29] In addition, the applicability of water-saturated [Hbet][Tf_2N] for studying the redox stability of neptunium and for separation of fission products was investigated for potential treatment of spent nuclear fuel. [30, 31] The extraction yield of some of these ions are shown in Table 1.

Table 1. The list of some metal ions that have been reported to be extracted into [Hbet][Tf_2N].

Metal of interest	**Aqueous phase media**	**Extraction yield**	**Reference**
Sc^{3+}	HCl or HNO_3	E > 95%	23
In^{3+} and Sc^{3+}	Water	D >200	24
La^{3+}, Pr^{3+}, Nd^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Ga^{3+}		10<D<200	
Eu^{3+}	HNO_3	D = 125	25

Ru^{3+}, Rh^{3+}, Pd^{2+}	HNO_3	$10<D<100$	26

Considering the wide applications of [Hbet][Tf_2N] and the potential use of its functionalized carboxylic acid group to extract metal ions, we decided to evaluate the extraction performance of an [Hbet][Tf_2N]-based extraction system to recover indium(III) and thallium(I, III) from hydrochloric acid solutions. There is a large interest for applications or recovery of these metals in many fields such as nuclear medicine; [32-34] hydrometallurgy and liquid crystal manufacturing; [35-37] and environmental protection. [38-40] In addition, there is also interest in exploring the partitioning behavior of In and Tl(I, III) into ionic liquids for a future investigation of their heavier homolog, nihonium. [41] The main goal of this current study is to understand the fundamental aspects of metal ion transfer into functionalized ionic liquid (focusing on indium and thallium behavior) and the corresponding mechanism of extraction into hydrophobic [Hbet][Tf_2N].

2. Experimental Section

2.1. Chemicals

High-purity grade betaine anhydrous (*N,N,N*–trimethylammonium acetate, abbreviated as betaine, ≥99.0%) and betaine hydrochloride (HbetCl, ≥99%) were purchased from Sigma (St. Louis, Missouri, USA). High-purity grade lithium *bis*(trifluoromethylsulfonyl)imide (Li[Tf_2N], ≥98.0%) salt was obtained from TCI America (Portland, Oregon, USA). Concentrated hydrochloric acid was purchased from Merck (Gernsheim, Darmstadt, Germany) and 70% (v/v) nitric acid was purchased from BDH chemicals (Sanborn, New York, USA). Both saturated 3% (w/v) bromine water and 0.3% (w/v) chlorine water were obtained from Ricca Chemical (Arlington, Texas, USA). Indium(III) chloride hydrate and thallium(III) chloride hydrate were of analytical grade and purchased from Alfa Aesar (Tewksbury, Massachusetts, USA). All chemical reagents were used as received without any further purification. Deionized water (ELGA PURELAB DV25) with a resistivity of 18.2 MΩ cm was used for preparing the aqueous solutions.

2.2. Radionuclides

Carrier-free ^{111}In and ^{201}Tl medical radioisotopes were purchased from Mallinckrodt (St. Louis, Missouri, USA). Table 2 shows the production methods and decay characteristics of the radionuclides.

Table 2. Radionuclides used in this work, decay characteristic and production methods. [42]

Nuclide	Nuclear reaction	Radiopurity (%)	Half-life (d)	γ Energy (keV)	Intensity (%)
^{111}In	^{112}Cd(p,2n)^{111}In	99.9	2.80	171.3	90.2
				245.5	94.0
^{201}Tl	^{203}Tl(p,3n)^{201}Pb → ^{201}Tl	98.2	3.04	70.8	46.0
				167.4	10.0

Indium(III) chloride in 0.05 M hydrochloric acid and thallium(I) chloride in 0.9% (w/v) sodium chloride and preserved with 0.9% (v/v) benzyl alcohol. The concentrations of ^{111}In and ^{201}Tl per sample after multistep dilution were below 1×10^{-11} M.

2.3. Sample preparation and analytical technique

Betainium *bis*(trifluoromethylsulfonyl)imide was synthesized following a procedure in the literature. [43] Due to its hygroscopic and viscous nature, this ionic liquid was saturated with pure water prior to the partition experiments. This step was essential to facilitate handling, to minimize changes in volume phase ratio, and to prevent further water uptake during the partition experiments.

The organic phase was prepared by weighing the water-saturated ionic liquid in a test tube to obtain a volume of 0.5 mL (density 1.439 ± 0.014 g/cm^3 at 23 ± 2 ^{o}C). [44] Subsequently, an equal volume of aqueous phase was added to the tube. In the absence of betaine, the aqueous phase was composed of only hydrochloric acid and an aliquot of indium or thallium stock solution. In the presence of betaine, it was composed of 15% (w/v) of betaine in hydrochloric acid and an aliquot of the metal ion (indium or thallium). This solution was prepared by weighing the appropriate amount of zwitterionic betaine in a tube and adding HCl into it volumetrically. In the case of Tl(III) extraction, an aliquot of bromine (Br_2) or chlorine (Cl_2) water was added in order to obtain Tl(III) in the solution, according to Ref. 45. Then, the biphasic system was shaken mechanically (VWR Signature digital vortex mixer) at 3000 rpm for 5 min (except for the kinetic study, in which the time was varied) at 23 ± 2^o C and centrifuged at 4400 rpm for 1 min (Eppendorf model 5702) in order to promote phase separation. Finally, an aliquot was taken from each phase to determine the indium or thallium concentration or activity. This procedure was implemented for extraction of indium and thallium(I, III) both in the absence and the presence of additional zwitterionic betaine.

The $Li[Tf_2N]$ stock solution was prepared by dissolving a known amount of $Li[Tf_2N]$ salt in 0.05 M HCl to the desired concentration. This stock solution was subsequently diluted in HCl solution to obtain various $Li[Tf_2N]$ concentrations.

A PerkinElmer automatic gamma counter with a NaI detector was used to determine the radionuclide activity level of both phases. The $Li[Tf_2N]$ dependency experiments (see Sec. 3.3 below) were performed using stable $InCl_3$ or $TlCl_3$ salt and the aqueous phase samples were analyzed using ICP-MS (PerkinElmer NexION 300D). The concentration of In and Tl(III) in the organic phase were determined by back-extraction with 2 M HCl. Most experiments were generally repeated twice and some were carried out in triplicate.

The metal ion distribution ratio, D_M, was determined by the following equation:

$$D_\mathrm{M} = \frac{\mathrm{A_{org}}}{\mathrm{A_{aq}}} \cdot \frac{\mathrm{V_{aq}}}{\mathrm{V_{org}}} \quad \mathrm{or} \quad D_\mathrm{M} = \frac{\mathrm{C_{org}}}{\mathrm{C_{aq}}} \qquad \mathrm{Eq.\ 1}$$

where A is count rate (counts per minute), C is concentration of analyte (M), and V is volume of each phase (mL). The subscripts “org” and “aq” denote metal species in the organic and aqueous phases, respectively. Throughout the text, the subscript “eq” refers to equilibrium conditions. Concentrations given in the text are expressed as molarities, M (mol/dm^3).

3. Results and discussion

3.1. Extraction kinetics

In order to evaluate the time necessary to reach equilibrium, the kinetics of In and Tl(III) extraction into water-saturated $[Hbet][Tf_2N]$ from dilute HCl solutions at room temperature was investigated and the results are plotted in Fig. 2. The partition of both In and Tl(III) between the two immiscible phases is very fast and extraction equilibrium is reached within 1 min. These results show that the traditional liquid-liquid extraction technique at room temperature is convenient for rapid metal transfer from HCl solutions into $[Hbet][Tf_2N]$.

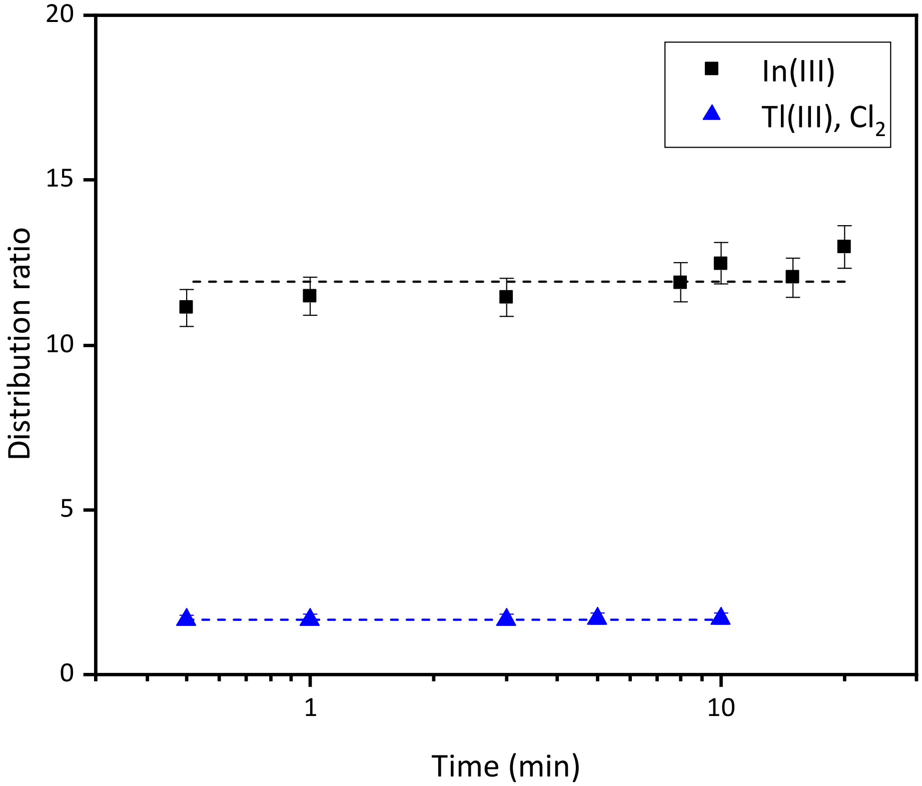

Fig. 2. The variation of D_{In} and $D_{Tl(III)}$ values as a function of mixing time. Trivalent indium and thallium were extracted into [Hbet][Tf_2N] from 0.01 M and 0.05 M HCl solutions, respectively. Chlorine water was used to oxidize thallium(I). The broken lines show the average D_{In} and $D_{Tl(III)}$ as a function of mixing time. Error bars represent statistical uncertainty only; for $D_{Tl(III)}$, they are smaller than the corresponding symbols used.

3.2. Effect of zwitterionic betaine

The addition of zwitterionic betaine as an extractant was shown to increase the extraction efficiency of metallic species. This is due to the presence of the deprotonated carboxyl group in the betaine structure which is able to coordinate with the metal ions. [24, 45] To determine the optimum betaine concentration suitable for indium and thallium extraction, different amounts of water-soluble zwitterionic betaine were added into the aqueous phase prior to phase contact.

Fig. 3a shows the variation of D_{In} values as a function of the aqueous concentration of betaine, where indium was extracted into [Hbet][Tf_2N] from 0.01 M HCl. The figure shows that D_{In} values are maximized at an initial aqueous betaine concentration of approximately 15 %

(w/v). It was observed visually that addition of higher amounts of betaine resulted in a more viscous aqueous phase and increased organic and aqueous phase miscibility (due to increasing [Hbet][Tf_2N] dissolution). [44] This is most likely the effect of the change in aqueous phase equilibria according to Le Châtelier's principle. The effect of adding higher amount of betaine was also studied; however, the phase separation was very poor. Addition of more than 20% (w/v) betaine into 0.01 M HCl aqueous phase leads to formation of monophasic system at room temperature. Therefore, there is not enough data to explain the decline that was observed in Fig. 3a.

Similar dependency of *D* values on the amount of betaine added was also observed in the case of thallium(I, III) extraction. As seen in Fig. 3b, the *D* values of thallium continuously increased with increasing betaine concentration with a more pronounced effect for Tl(III). However, the presence of higher acid concentrations in the thallium extraction system (0.2 M compared to 0.01 M in the indium extraction system) increased the level of betaine protonation and reduced phase miscibility. Consequently, the *D* values of thallium increased even with the addition of 20% (w/v) betaine in the aqueous phase.

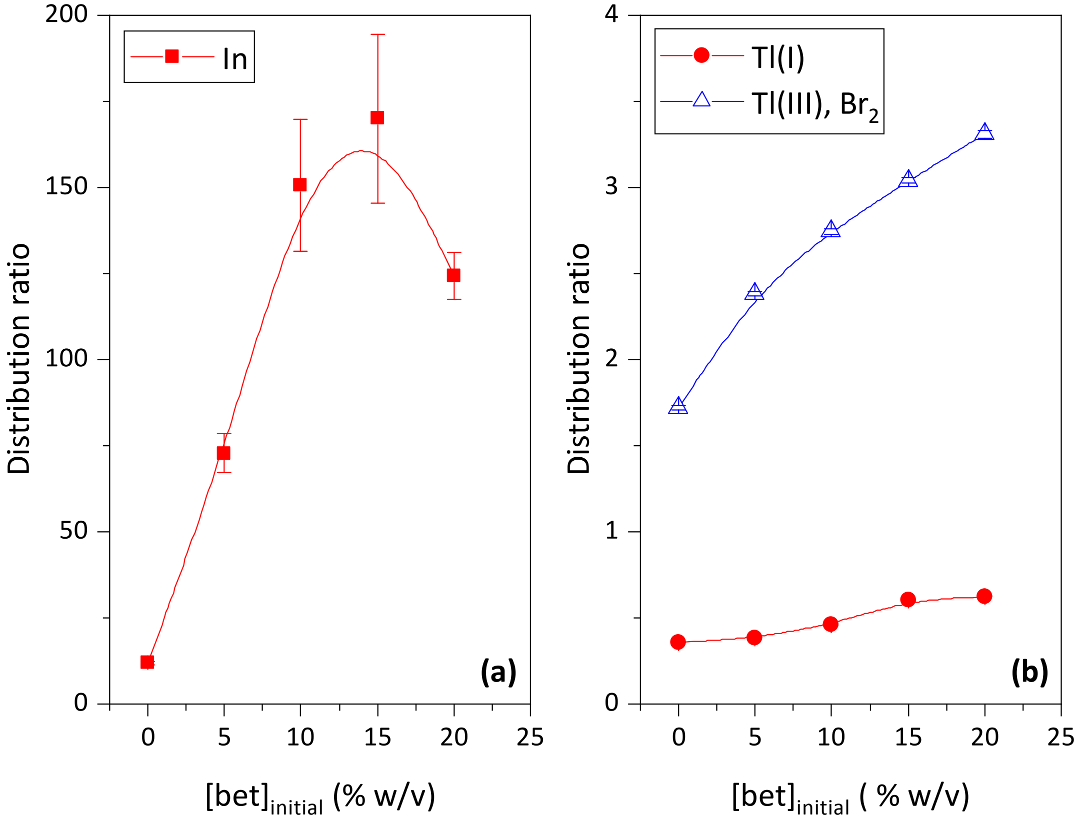

Fig. 3. Distribution ratio of metals extracted into [Hbet][Tf_2N] as a function of initial added betaine concentration: **(a)** indium extracted from 0.01 M HCl, **(b)** thallium extracted from 0.2 M HCl; error bars represent statistical uncertainty only and are smaller than the corresponding symbols. Thallium was oxidized using bromine water. The lines are drawn to guide the eye.

3.3. Li[Tf_2N] dependency

The dependency of In and Tl(III) extraction on the ionic liquid's anion concentration in the aqueous phase was investigated. This study was aimed to determine the role of [Tf_2N^-] anions in the extraction of these metals and was done by adding Li[Tf_2N] salt into the aqueous acidic phase ($[HCl]_{aq,\ init}$ = 0.05 M). The initial concentration of the salt was varied in the range of 0.004 – 0.6 M. The obtained results are presented in Fig. 4.

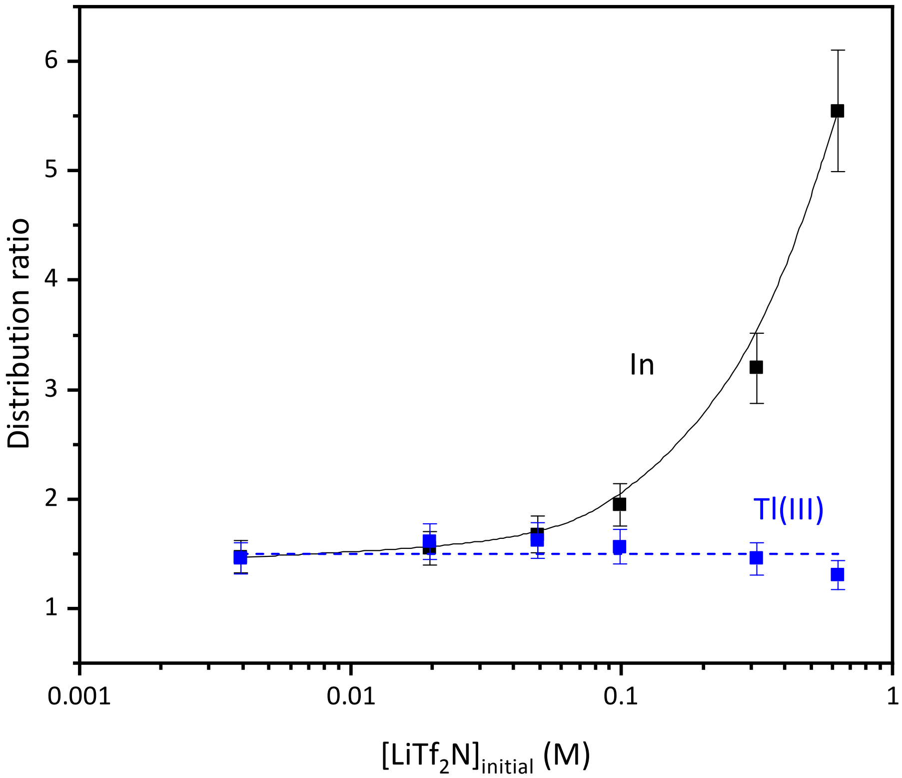

Fig. 4. The dependency of In and Tl(III) extraction on the Li[Tf_2N] initial concentration in the aqueous phase (0.05 M HCl). Thallium(I) was oxidized by using chlorine water. The broken line is the average value of $D_{Tl(III)}$, while the solid line is drawn to guide the eye. Error bars only represent statistical uncertainty.

The extraction of In shows an increasing trend of D_{In} values with increasing [Tf_2N^-] concentration. This suggests that indium most likely exists as cationic species at 0.05 M HCl and the presence of [Tf_2N^-] promotes the extraction of this species. On the other hand, addition of Li[Tf_2N] has no effect on thallium(III) behavior as there is no significant changes observed in the presence of this salt. This result indicates that Tl(III) predominantly exists as a cationic species in the aqueous phase and [Tf_2N^-] is not involved in Tl(III) extraction. Suggested speciation of indium and trivalent thallium under described experimental conditions is in agreement with literature data. [46] The extraction mechanism of these metal species will be considered below.

3.4. Effect of HCl concentration

The next step was to study the ability of water-saturated [Hbet][Tf_2N] to extract In, Tl(I) and Tl(III) from aqueous hydrochloric acid solutions in the absence and presence of zwitterionic betaine. Since it was found that the extraction of indium was maximized when 15% (w/v) of betaine was added into the aqueous phase, the acid dependency of both indium and thallium extraction was investigated with the addition of this amount of betaine.

Figure 5 shows the dependency of distribution ratio of In on the initial aqueous HCl concentration, with and without the presence of betaine. As can be seen in both systems, increasing acid concentration reduced D_{In} values in the entire HCl range. The distribution ratios of In are reaching 0.01 in elevated HCl concentrations, indicating metal retention in the aqueous phase. When 15% (w/v) of betaine is present in the system, D_{In} values decrease more steeply in 0.2 – 3 M HCl compared to the system without betaine. However, at higher acid concentrations, the addition of betaine did not affect indium extraction significantly.

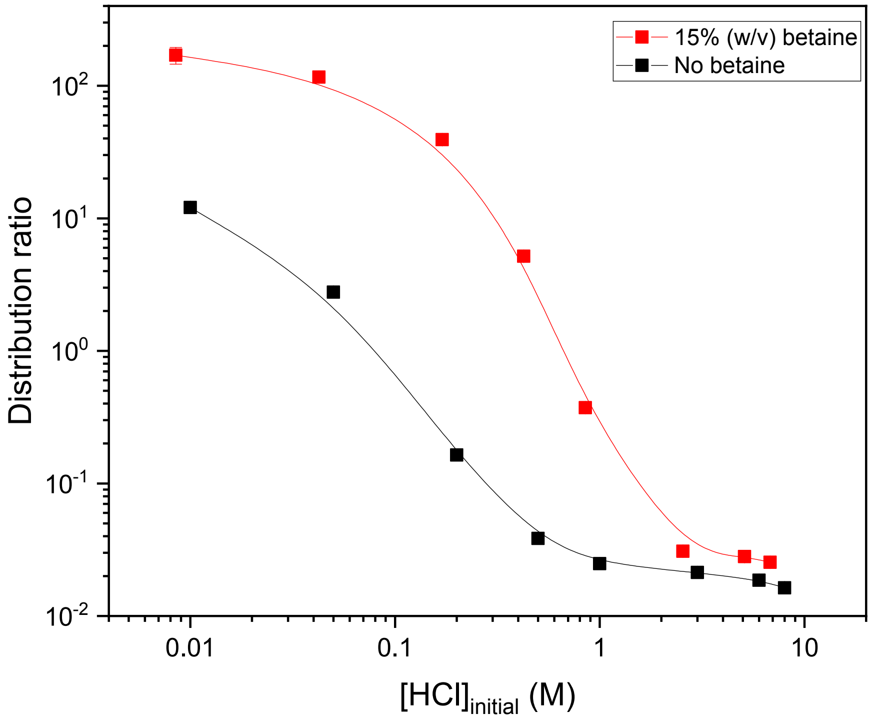

Fig. 5. The distribution ratio of indium extracted into $[Hbet][Tf_2N]$ ionic liquid as the function of initial aqueous HCl concentration in the absence and presence of 15% (w/v) zwitterionic betaine. Error bars on D_{In} in the absence of betaine represent statistical uncertainty only. In both plots, the error bars are smaller than the corresponding symbols. The solid lines are drawn to guide the eye.

Similarly, the extraction of Tl(I) and Tl(III) also shows dependency on the aqueous phase acidity. As shown in Fig. 6, the *D* values for both Tl(I) and Tl(III) gradually decrease under acidic conditions. In the system without betaine added, the distribution ratios of Tl(III) show a minor decrease up to 1 M HCl, regardless what oxidizing agent was used (Fig. 6a). Generally, *D* values are greater when thallium was oxidized using Br_2 water than Cl_2 water. This is due to the higher stability and hydrophobicity of mixed thallium chloro- and bromocomplexes than pure chlorocomplexes. [47, 48] Above 1 M HCl, the decline of *D* values is more pronounced with no difference between oxidizers; this is most likely due to the presence of only thallium chloro complexes in the aqueous phase. Similar behavior was observed in our previous paper where we believe that Cl^- anions displace Br^- in thallium complexes in concentrated HCl. [47] On the other hand, Tl(I) stays in the aqueous phase due to its high hydrophilicity and insignificant partitioning to $[Hbet][Tf_2N]$ over the entire range of HCl concentrations (Fig. 6b).

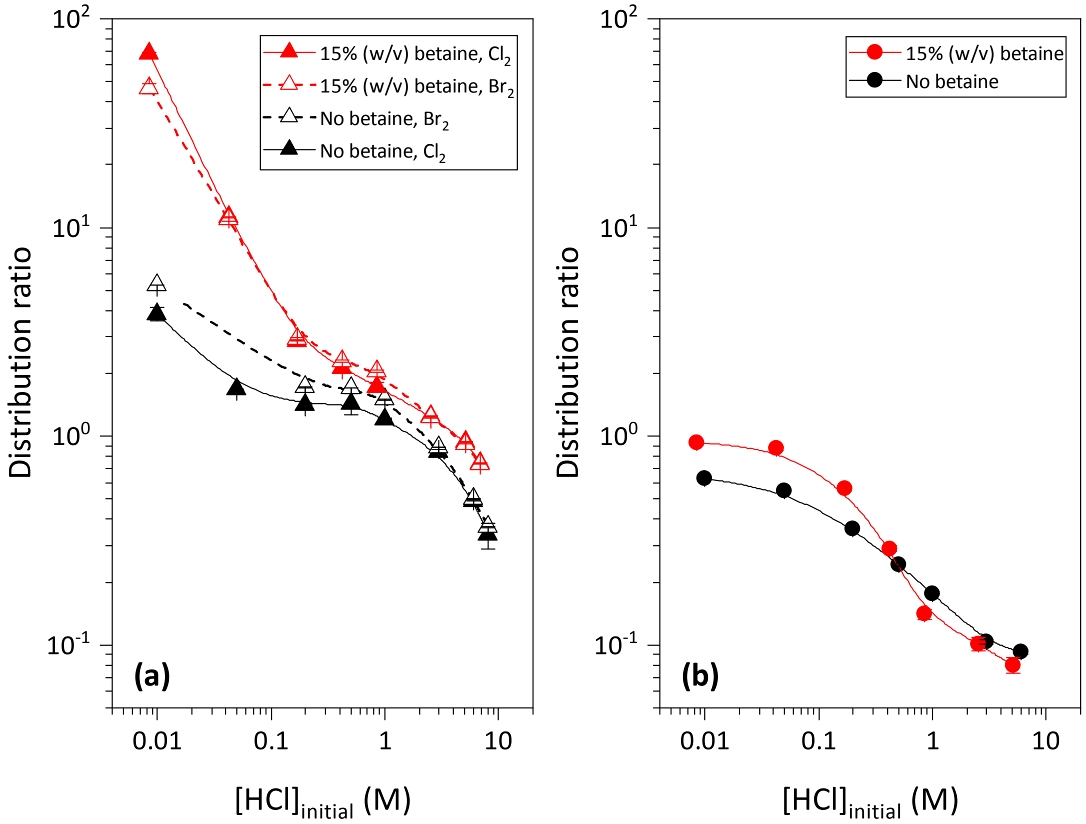

Fig. 6. The distribution ratio of thallium extracted into [Hbet][Tf_2N] ionic liquid as a function of initial aqueous HCl concentration in the absence and presence of 15% (w/v) zwitterionic betaine: **(a)** extraction of thallium(III) using Cl_2 water or Br_2 water as the oxidizing agent, **(b)** extraction of thallium(I). The lines are drawn to guide the eye. Error bars represent statistical uncertainty only and are smaller than the corresponding symbols.

In the presence of 15% (w/v) betaine, at any given HCl concentration in the range of 0.01 – 0.2 M, $D_{Tl(III)}$ is higher compared to the system without betaine added (Fig. 6a). Above 0.2 M HCl, the difference in $D_{Tl(III)}$ between the systems with or without betaine added is not significant (especially if the 10% systematic experimental uncertainty is taken into account). In general, $D_{Tl(III)}$ decreased with increasing aqueous phase acidity and almost no difference in $D_{Tl(III)}$ values was observed when Br_2 water or Cl_2 water was used to oxidized thallium. Similar behavior was also observed on Tl(I) extraction in this system (Fig. 6b). Addition of betaine increased the extraction yield of thallium(I) in the same acid region but to a lesser extent compared to thallium(III). Above 0.5 M HCl, $D_{Tl(I)}$ is comparable with the value in the absence of betaine. This suggests that betaine does not participate in the extraction of Tl(III) or Tl(I) at high acidity.

3.5. Mechanism of extraction

It is known that the presence of HCl acid affects the speciation of the metals as well as the solubility of [Hbet][Tf_2N], dissociation of its cation in the aqueous phase, and protonation of its anion. [23, 42, 44, 47, 49-51] In addition, it has been shown that the presence of betaine in a [Hbet][Tf_2N]-HCl mixture prompted the transfer of betaine species into the organic phase and increased the solubility of [Hbet][Tf_2N] in the aqueous phase. [44]

On this basis, we developed mathematical models to explain the extraction mechanism of In and Tl into [Hbet][Tf_2N]. We believe several mechanisms may be considered:

a) Ion pair formation with [Tf_2N^-];
b) Ion pair formation with [$Hbet^+$];
c) Cation exchange and
d) Anion exchange.

3.5.1. Ion pair formation with [Tf_2N^-]

First, the mechanism of ion pair formation with [Tf_2N^-] is considered. We believe that a two-step process occurs where the positively charged halide complexes interact with the ionic liquid's cation dissolved in the aqueous phase (Eq. 2), followed by the extraction of the betaine-containing complex paired with the IL anion into the organic phase (Eq. 3). For In and Tl(III), the generic reactions can be written as follows, assuming that betaine is a monodentate ligand:

$$\mathrm{ML_y}^{3-\mathrm{y}}{}_{\mathrm{aq}} + \mathrm{x}\,[\mathrm{Hbet}^+]_{\mathrm{aq}} \rightleftarrows \mathrm{ML_y(bet)_x}^{3-\mathrm{y}}{}_{\mathrm{aq}} + \mathrm{x}\,\mathrm{H}^+{}_{\mathrm{aq}} \qquad \text{Eq. 2}$$

$$\mathrm{ML_y(bet)_x}^{3-\mathrm{y}}{}_{\mathrm{aq}} + (3-\mathrm{y})\,[\mathrm{Tf_2N}^-]_{\mathrm{aq}} \rightleftarrows [\mathrm{ML_y(bet)_x}][(\mathrm{Tf_2N})_{3-\mathrm{y}}]_{\mathrm{org}} \qquad \text{Eq. 3}$$

where M represents the trivalent indium or thallium metal, L represents the inorganic ligand (*i.e.*, Cl^-), $0 \leq y \leq 2$ to deal with positively charged halide complexes and $0 \leq x \leq 6$ (since the number of ligands cannot exceed 6, which is the coordination number of In/Tl(III), $x + y \leq 6$). [49, 52-54]

The equilibrium constant of the reaction in Eq. 2 can be written as:

$$\mathrm{K_{M(III)}} = \frac{[\mathrm{ML_y(bet)_x}^{3-\mathrm{y}}]_{\mathrm{aq}} \cdot (a_{\mathrm{H}^+})^{\mathrm{x}}{}_{\mathrm{aq}}}{[\mathrm{ML_y}^{3-\mathrm{y}}]_{\mathrm{aq}} \cdot [\mathrm{Hbet}^+]^{\mathrm{x}}{}_{\mathrm{aq}}} \qquad \text{Eq. 4}$$

where M(III) is either In or Tl(III). The activity of proton, a_{H^+}, in Eq. 4 is defined as:

$$a_{\mathrm{H}^+} = \gamma_{HCl\pm} \cdot [\mathrm{H}^+] \qquad \text{Eq. 5}$$

Considering that the data on the activity coefficient of the protons is limited and does not cover the entire range of HCl used in this work, [55, 56] the mean activity coefficient of HCl, $\gamma_{\mathrm{HCl}\pm}$, in Eq. 5 is used as an approximation. This quantity was obtained using a lookup table based on literature data combined with linear interpolation. [44, 57] Unfortunately, the activity coefficients of the ionic liquid species ($[\mathrm{Hbet}^+]$ and $[\mathrm{Tf_2N}^-]$) are unknown and are not included in the mathematical models developed for this work.

Combining Eqs. 2 and 3, one can express the extraction constant of ion pair formation, $\mathrm{K}_{\mathrm{ext\_IP}^-}$:

$$\mathrm{K}_{\mathrm{ext\_IP}^-\ \mathrm{M(III)}} = \frac{[\mathrm{ML_y(bet)_x}][(\mathrm{Tf_2N})_{3-y}]_{\mathrm{org}} \cdot (a_{\mathrm{H}^+})^{\mathrm{x}}{}_{\mathrm{aq}}}{\mathrm{K_{M(III)}} \cdot [\mathrm{ML_y}^{3-y}]_{\mathrm{aq}} \cdot [\mathrm{Hbet}^+]^{\mathrm{x}}{}_{\mathrm{aq}} \cdot [\mathrm{Tf_2N}^-]^{3-y}{}_{\mathrm{aq}}} \qquad \text{Eq. 6}$$

Similarly, the ion pair formation mechanism for extraction of positively charged Tl(I) can be written as follows:

$$\mathrm{Tl^+}_{\mathrm{aq}} + \mathrm{x}\,[\mathrm{Hbet}^+]_{\mathrm{aq}} \rightleftarrows \mathrm{Tl(bet)_x}^+{}_{\mathrm{aq}} + \mathrm{x\,H^+}_{\mathrm{aq}} \qquad \text{Eq. 7.}$$

$$\mathrm{Tl(bet)_x}^+{}_{\mathrm{aq}} + [\mathrm{Tf_2N}^-]_{\mathrm{aq}} \rightleftarrows [\mathrm{Tl(bet)_x}][\mathrm{Tf_2N}]_{\mathrm{org}} \qquad \text{Eq. 8}$$

where $0 \leq x \leq 4$ (since the number of ligands cannot exceed 4, which is the coordination number of Tl(I)). [58] Therefore,

$$\mathrm{K_{Tl(I)}} = \frac{[\mathrm{Tl(bet)_x}^+]_{\mathrm{aq}} \cdot (a_{\mathrm{H}^+})^{\mathrm{x}}{}_{\mathrm{aq}}}{[\mathrm{Tl}^+]_{\mathrm{aq}} \cdot [\mathrm{Hbet}^+]^{\mathrm{x}}{}_{\mathrm{aq}}} \qquad \text{Eq. 9}$$

$$\mathrm{K}_{\mathrm{ext\_IP}^-\ \mathrm{Tl(I)}} = \frac{[\mathrm{Tl(bet)_x}][\mathrm{Tf_2N}]_{\mathrm{org}} \cdot (a_{\mathrm{H}^+})^{\mathrm{x}}{}_{\mathrm{aq}}}{\mathrm{K_{Tl(I)}} \cdot [\mathrm{Tl}^+]_{\mathrm{aq}} \cdot [\mathrm{Hbet}^+]^{\mathrm{x}}{}_{\mathrm{aq}} \cdot [\mathrm{Tf_2N}^-]_{\mathrm{aq}}} \qquad \text{Eq. 10}$$

Expressing Eqs. 6 and 10 in terms of the distribution ratio leads to:

$$\mathrm{D}_{\mathrm{IP}^-\ \mathrm{M(III)}} = \frac{\mathrm{C}_{\mathrm{ext\_IP}^-} \cdot [\mathrm{Hbet}^+]^{\mathrm{x}}{}_{\mathrm{aq}} \cdot [\mathrm{Tf_2N}^-]^{3-y}{}_{\mathrm{aq}}}{(a_{\mathrm{H}^+})^{\mathrm{x}}{}_{\mathrm{aq}}} \qquad \text{Eq. 11}$$

$$\mathrm{D}_{\mathrm{IP}^-\ \mathrm{Tl(I)}} = \frac{\mathrm{C}_{\mathrm{ext\_IP}^-} \cdot [\mathrm{Hbet}^+]^{\mathrm{x}}{}_{\mathrm{aq}} \cdot [\mathrm{Tf_2N}^-]_{\mathrm{aq}}}{(a_{\mathrm{H}^+})^{\mathrm{x}}{}_{\mathrm{aq}}} \qquad \text{Eq. 12}$$

where *D* is the metallic species ratio in both phases according to Eq. 1. The value *x* obtained from Eq. 11 and 12 is the number of betaine molecules that formed a complex with the metallic species (Eq. 2 or 7). The value $\mathrm{C}_{\mathrm{ext\_IP}^-}$ is equal to $\mathrm{K}_{\mathrm{ext\_IP}^-\ \mathrm{M(III)}} \cdot \mathrm{K_{M(III)}}$ for In and Tl(III) or $\mathrm{K}_{\mathrm{ext\_IP}^-\ \mathrm{Tl(I)}} \cdot \mathrm{K_{Tl(I)}}$ for Tl(I).

3.5.2. Ion pair formation with [Hbet⁺]

Ion pair formation between negatively charged halide complexes and the IL cation is also potentially possible. In this case the generic chemical reaction for In and Tl(III), after Eq. 2 is complete, would be:

$$\mathrm{ML_y(bet)_x}{}^{3-\mathrm{y}}{}_{\mathrm{aq}} + (\mathrm{y}-3)[\mathrm{Hbet}^+]_{\mathrm{aq}} \rightleftarrows [\mathrm{Hbet}]_{\mathrm{y}-3}[\mathrm{ML_y(bet)_x}]_{\mathrm{org}} \qquad \text{Eq. 13}$$

where 4 ≤ y ≤ 6 since the halide complexes must be negatively charged and 0 ≤ x ≤ 2 (the coordination number of In/Tl(III) is 6, since we consider anionic complexes with number of ligands between 4 – 6, the number of betaine that can potentially coordinate with the metal ion is limited to 0 – 2, x + y ≤ 6). [49, 52-54]

For Tl(I),

$$\mathrm{TlL_y(bet)_x}{}^{1-\mathrm{y}}{}_{\mathrm{aq}} + (\mathrm{y}-1)\ [\mathrm{Hbet}^+]_{\mathrm{aq}} \rightleftarrows [\mathrm{Hbet}]_{\mathrm{y}-1}[\mathrm{TlL_y(bet)_x}]_{\mathrm{org}} \qquad \text{Eq. 14.}$$

where 2 ≤ y ≤ 4 since the halide complexes must be negatively charged and 0 ≤ x ≤ 2 (the coordination number of Tl(I) is 4, since we consider anionic complexes with number of ligands between 2 – 4, the number of betaine that can potentially coordinate with the metal ion is limited to 0 – 2, x + y ≤ 4). [58]

The corresponding extraction constants, taking Eq. 4 into account, may be expressed as:

$$\mathrm{K_{ext\_IP^+\ M(III)}} = \frac{[\mathrm{Hbet}^+]_{\mathrm{y}-3}[\mathrm{ML_y(bet)_x}]_{\mathrm{org}} \cdot (a_{\mathrm{H}^+})^{\mathrm{x}}{}_{\mathrm{aq}}}{\mathrm{K_{M(III)}} \cdot [\mathrm{ML_y}{}^{3-\mathrm{y}}]_{\mathrm{aq}} \cdot [\mathrm{Hbet}^+]^{\mathrm{y}-3+\mathrm{x}}{}_{\mathrm{aq}}} \qquad \text{Eq. 15}$$

$$\mathrm{K_{ext\_IP^+\ Tl(I)}} = \frac{[\mathrm{Hbet}^+]_{\mathrm{y}-1}[\mathrm{TlL_y(bet)_x}]_{\mathrm{org}} \cdot (a_{\mathrm{H}^+})^{\mathrm{x}}{}_{\mathrm{aq}}}{\mathrm{K_{Tl(I)}} \cdot [\mathrm{TlL_y}{}^{1-\mathrm{y}}]_{\mathrm{aq}} \cdot [\mathrm{Hbet}^+]^{\mathrm{y}-1+\mathrm{x}}{}_{\mathrm{aq}}} \qquad \text{Eq. 16}$$

The form of these equations in terms of *D* is again

$$\mathrm{D_{IP^+\ M(III)}} = \frac{\mathrm{C_{ext\_IP^+}} \cdot [\mathrm{Hbet}^+]^{\mathrm{y}-3+\mathrm{x}}{}_{\mathrm{aq}}}{(a_{\mathrm{H}^+})^{\mathrm{x}}{}_{\mathrm{aq}}} \qquad \text{Eq. 17}$$

$$\mathrm{D_{IP^+\ Tl(I)}} = \frac{\mathrm{C_{ext\_IP^+}} \cdot [\mathrm{Hbet}^+]^{\mathrm{y}-1+\mathrm{x}}{}_{\mathrm{aq}}}{(a_{\mathrm{H}^+})^{\mathrm{x}}{}_{\mathrm{aq}}} \qquad \text{Eq. 18}$$

and the value $\mathrm{C_{ext\_IP^+}}$ is equal to $\mathrm{K_{ext\_IP^+\ Tl(III)}} \cdot \mathrm{K_{M(III)}}$ for In and Tl(III) and $\mathrm{K_{ext\_IP^+\ Tl(I)}} \cdot \mathrm{K_{Tl(I)}}$ for Tl(I).

3.5.3. Cation exchange

Another possible extraction mechanism is cation exchange. The following model assumes that the positively charged trivalent indium or thallium cations or halo complexes are exchanged with the betainium cation from the ionic liquid after the reaction described by Eq. 2 has occurred:

$$\mathrm{ML_y(bet)_x}^{3-\mathrm{y}}{}_{\mathrm{aq}} + (3-\mathrm{y})[\mathrm{Hbet}^+]_{\mathrm{org}} \rightleftarrows \mathrm{ML_y(bet)_x}^{3-\mathrm{y}}{}_{\mathrm{org}} + (3-\mathrm{y})[\mathrm{Hbet}^+]_{\mathrm{aq}} \quad \text{Eq. 19}$$

where 0 ≤ y ≤ 2 since the halide complexes must be positively charged and 0 ≤ x ≤ 6 (see Sec. 3.5.1 for details). The extraction constant for cation exchange in the reaction above, taking Eq. 4 into account, is:

$$\mathrm{K_{ext\_CE\ M(III)}} = \frac{[\mathrm{ML_y(bet)_x}^{3-\mathrm{y}}]_{\mathrm{org}} \cdot [\mathrm{Hbet}^+]^{3-\mathrm{y}-\mathrm{x}}{}_{\mathrm{aq}} \cdot (a_{\mathrm{H}^+})^{\mathrm{x}}{}_{\mathrm{aq}}}{\mathrm{K_{M(III)}} \cdot [\mathrm{ML_y}^{3-\mathrm{y}}]_{\mathrm{aq}}} \quad \text{Eq. 20}$$

The extraction mechanism of monovalent thallium through the cation exchange can be expressed after Eq. 7 is complete:

$$\mathrm{Tl(bet)_x}^+{}_{\mathrm{aq}} + [\mathrm{Hbet}^+]_{\mathrm{org}} \rightleftarrows \mathrm{Tl(bet)_x}^+{}_{\mathrm{org}} + [\mathrm{Hbet}^+]_{\mathrm{aq}} \quad \text{Eq. 21}$$

where 0 ≤ x ≤ 4 (see Sec. 3.5.1 for details).

$$\mathrm{K_{ext\_CE\ Tl(I)}} = \frac{[\mathrm{Tl(bet)_x}^+]_{\mathrm{org}} \cdot [\mathrm{Hbet}^+]^{1-x}{}_{\mathrm{aq}} \cdot (a_{\mathrm{H}^+})^{\mathrm{x}}{}_{\mathrm{aq}}}{\mathrm{K_{Tl(I)}} \cdot [\mathrm{Tl}^+]_{\mathrm{aq}}} \quad \text{Eq. 22}$$

The equations in terms of *D* for In and Tl(III) (Eq. 17) and for Tl(I) (Eq. 19) are

$$\mathrm{D_{CE\ M(III)}} = \frac{\mathrm{C_{ext\_CE}}}{[\mathrm{Hbet}^+]^{3-\mathrm{y}-\mathrm{x}}{}_{\mathrm{aq}} \cdot (a_{\mathrm{H}^+})^{\mathrm{x}}{}_{\mathrm{aq}}} \quad \text{Eq. 23}$$

$$\mathrm{D_{CE\ Tl(I)}} = \frac{\mathrm{C_{ext\_CE}}}{[\mathrm{Hbet}^+]^{1-x}{}_{\mathrm{aq}} \cdot (a_{\mathrm{H}^+})^{\mathrm{x}}{}_{\mathrm{aq}}} \quad \text{Eq. 24}$$

and in this case the value $\mathrm{C_{ext\_CE}}$ for In and Tl(III) is equal to $\mathrm{K_{ext\_CE\ M(III)}} \cdot \mathrm{K_{Tl(III)}}$ and for Tl(I) is equal to $\mathrm{K_{ext\_CE\ Tl(I)}} \cdot \mathrm{K_{Tl(I)}}$.

3.5.4. Anion exchange

Since it is known that the metals considered can also form anionic complexes in aqueous hydrochloric acid solution, [49, 58, 59] the possibility of extraction of the negatively charged metal complexes through an anion exchange mechanism, after Eq. 2 is complete, is also considered:

$$\mathrm{ML_y(bet)_x}^{3-\mathrm{y}}{}_{\mathrm{aq}} + (\mathrm{y}-3)[\mathrm{Tf_2N}^-]_{\mathrm{org}} \rightleftarrows \mathrm{ML_y(bet)_x}^{3-\mathrm{y}}{}_{\mathrm{org}} + (\mathrm{y}-3)[\mathrm{Tf_2N}^-]_{\mathrm{aq}} \quad \text{Eq. 25}$$

where $4 \leq y \leq 6$ since the halide complexes must be negatively charged and $0 \leq x \leq 2$ (see Sec. 3.5.2 for details). The extraction constant for anion exchange in the reaction above, taking Eq. 4 into account, is:

$$\mathrm{K}_{\mathrm{ext\_AE\ M(III)}} = \frac{\left[\mathrm{ML_y(bet)_x}^{3-y}\right]_{\mathrm{org}} \cdot \left[\mathrm{Tf_2N^-}\right]^{y-3}{}_{\mathrm{aq}} \cdot \left(a_{\mathrm{H^+}}\right)^{x}{}_{\mathrm{aq}}}{\mathrm{K}_{\mathrm{M(III)}} \cdot \left[\mathrm{ML_y}^{3-y}\right]_{\mathrm{aq}} \cdot \left[\mathrm{Hbet^+}\right]^{x}{}_{\mathrm{aq}}} \qquad \text{Eq. 26}$$

Similarly, the extraction of monovalent thallium through anion exchange can be expressed as:

$$\mathrm{TlL_y(bet)_x}^{1-y}{}_{\mathrm{aq}} + (y-1)\left[\mathrm{Tf_2N^-}\right]_{\mathrm{org}} \rightleftarrows \mathrm{TlL_y(bet)_x}^{1-y}{}_{\mathrm{org}} + (y-1)\left[\mathrm{Tf_2N^-}\right]_{\mathrm{aq}} \qquad \text{Eq. 27}$$

where $2 \leq y \leq 4$ since the halide complexes must be negatively charged and $0 \leq x \leq 2$ (see Sec. 3.5.2 for details).

$$\mathrm{K}_{\mathrm{ext\_AE\ Tl(I)}} = \frac{\left[\mathrm{TlL_y(bet)_x}^{1-y}\right]_{\mathrm{org}} \cdot \left[\mathrm{Tf_2N^-}\right]^{y-1}{}_{\mathrm{aq}} \cdot \left(a_{\mathrm{H^+}}\right)^{x}{}_{\mathrm{aq}}}{\mathrm{K}_{\mathrm{Tl(I)}} \cdot \left[\mathrm{Tl^+}\right]_{\mathrm{aq}} \cdot \left[\mathrm{Hbet^+}\right]^{x}{}_{\mathrm{aq}}} \qquad \text{Eq. 28}$$

The equations in terms of *D* are

$$\mathrm{D}_{\mathrm{AE\ M(III)}} = \frac{\mathrm{C}_{\mathrm{ext\_AE}} \cdot \left[\mathrm{Hbet^+}\right]^{x}{}_{\mathrm{aq}}}{\left[\mathrm{Tf_2N^-}\right]^{y-3}{}_{\mathrm{aq}} \cdot \left(a_{\mathrm{H^+}}\right)^{x}{}_{\mathrm{aq}}} \qquad \text{Eq. 29}$$

$$\mathrm{D}_{\mathrm{AE\ Tl(I)}} = \frac{\mathrm{C}_{\mathrm{ext\_AE}} \cdot \left[\mathrm{Hbet^+}\right]^{x}{}_{\mathrm{aq}}}{\left[\mathrm{Tf_2N^-}\right]^{y-1}{}_{\mathrm{aq}} \cdot \left(a_{\mathrm{H^+}}\right)^{x}{}_{\mathrm{aq}}} \qquad \text{Eq. 30}$$

and the value $\mathrm{C}_{\mathrm{ext\_AE}}$ for In and Tl(III) is equal to $\mathrm{K}_{\mathrm{ext\_AE\ M(III)}} \cdot \mathrm{K}_{\mathrm{Tl(III)]}}$ and for Tl(I) is equal to $\mathrm{K}_{\mathrm{ext\_CE\ [Tl(I)]}} \cdot \mathrm{K}_{\mathrm{Tl(I)}}$.

3.5.5. Comparison of proposed mechanisms

All final equations should be considered as a function of *D* = f($a_{\mathrm{H^+}}$), where dependencies of [Hbet$^+$] and [Tf$_2$N$^-$] on $a_{\mathrm{H^+}}$ were characterized (see Fig. 7) in our previous paper.[44] Based on the proposed models, the fit of experimental data was performed to determine the most likely extraction mechanism for In, Tl(I), and Tl(III).

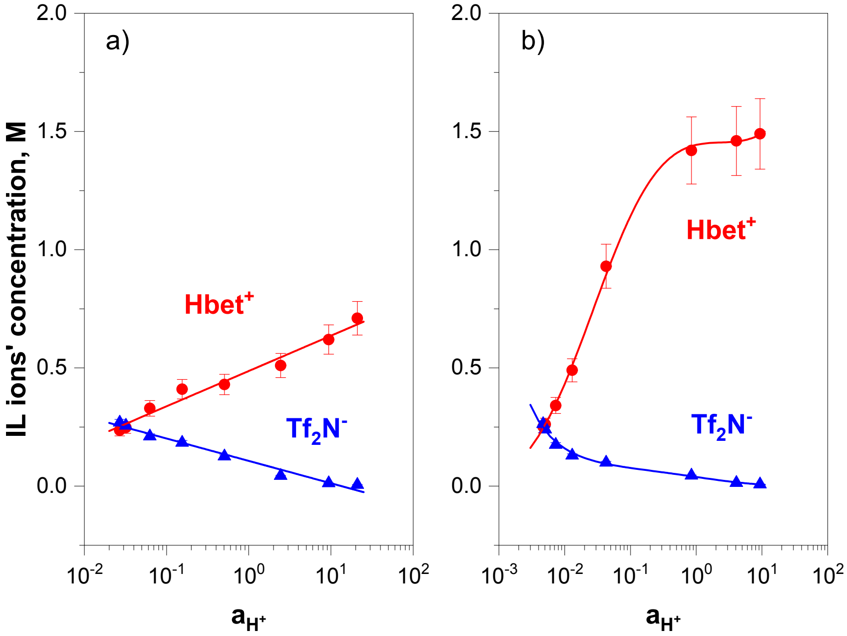

Fig. 7. The plot of Hbet$^+$ and Tf$_2$N$^-$ aqueous equilibrium concentrations versus a_{H^+} in the absence **(a)** and presence of 15% (w/v) betaine **(b)**. The data are taken from our previous paper.[44]

In some cases we were only able to estimate the value of K$_{ext}$ · K. However, if *x* = 0, then according to our models, the extracted metal complex does not contain betaine and the reactions shown in Eqs. 2 and 7 did not occur. Consequently, the constants $K_{[In,\ Tl(III)]}$ and $K_{Tl(I)}$ are no longer relevant and we can estimate the value of K$_{ext}$. To simplify our calculations, a set of integer values *x* and *y* was used according to the ligand range per each mechanism considered (see Sec. 3.5.1 – 3.5.4). It must be noted that equations considered above are applicable if there is only one metal species present in a given HCl range.

As the first step to determine the dominant extraction mechanism of each metal ion, we took into account the known metal speciation in the acid region of interest. Then, we chose the largest possible value of the product K$_{ext}$ · K (where K$_{ext}$ represents the extraction constant of a particular mechanism and K is the formation constant of the extractable metal complex) for each of the proposed mechanisms. These two factors were used as an indication of the most possible extraction pathway, provided that the result is consistent with the known chemistry of the metal of interest.

Figure 8 shows the plot of the distribution ratio values of In as a function of the hydrogen ion activity according to the relevant equations in the models above.

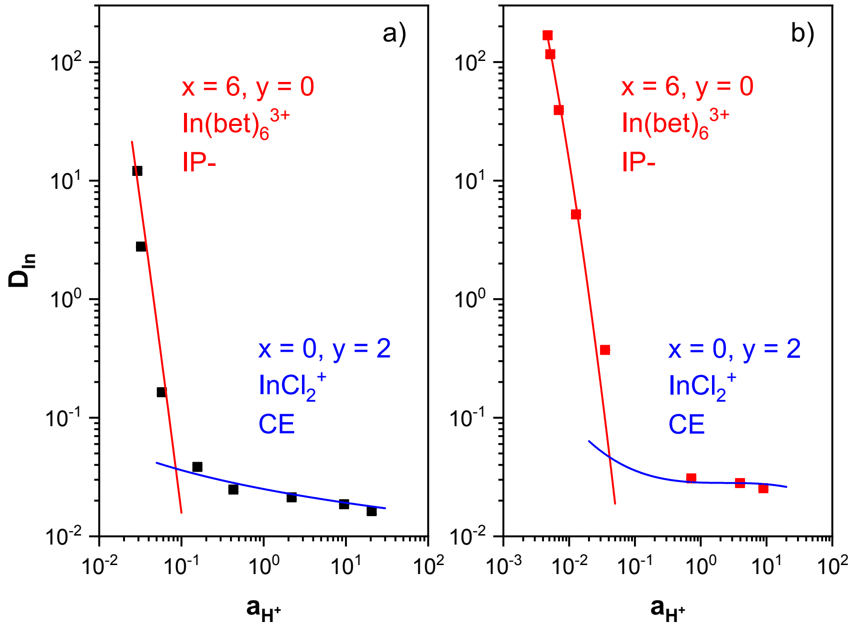

Fig. 8. The plot of D_{In} versus a_{H^+} in the absence **(a)** and presence of 15% (w/v) betaine **(b)**. The lines are results of fitting according to equations in sections 3.5.1 – 3.5.4. In both plots, the error bars are smaller than the corresponding symbols.

The calculated $K_{ext\ In} \cdot K_{In}$ values at lower acidity (a_{H^+} < 0.1) for all applicable mechanisms that we considered above are listed in Table 3. There are two competing mechanisms for cationic indium species, [60] namely ion pair formation with [Tf_2N^-] and cation exchange. The best fit was found for x = 6 and y = 0. The estimated constant product suggests that the former mechanism is a predominant one because the calculated values for the ion pair formation mechanism are at least three orders of magnitude greater than those for cation exchange. Thus, the extracted species is [In(bet)$_6$][Tf_2N]$_3$. This is supported by our finding in Fig. 4, where the increase of [Tf_2N^-] concentration in the 0.05 M HCl aqueous phase led to a more efficient extraction of indium.

Table 3. Estimated values of $K_{ext\ In} \cdot K_{In}$ for a_{H^+} < 0.1 region (x = 6 and y = 0).

In(bet)$_6^{3+}$		
Mechanism	**Absence of betaine**	**15% (w/v) betaine**

$K_{ext\_IP^- \ In} \cdot K_{In}$	$(1.3 \pm 0.3) \cdot 10^{-3}$	$(5.59 \pm 0.19) \cdot 10^{-7}$
$K_{ext\_CE\ In} \cdot K_{In}$	$(3.6 \pm 0.8) \cdot 10^{-7}$	$(1.255 \pm 0.016) \cdot 10^{-10}$

Table 4. Estimated values of $K_{ext\ In}$ at high acidity range (*x* = 0 and *y* = 2).

$InCl_2^+$		
Mechanism	**Absence of betaine**	**15% (w/v) betaine**
$K_{ext\_CE\ In}$	$(1.22 \pm 0.07) \cdot 10^{-2}$	$(4.10 \pm 0.18) \cdot 10^{-2}$

The data calculated at higher acid concentration for both chemical systems with and without betaine added are shown in Table 4. The best fit was found for *x* = 0 and *y* = 2. As mentioned previously, the constant K_{In} is irrelevant when *x* = 0; therefore, Table 4 shows the calculated $K_{ext\ In}$. The only mechanism that explains the indium behavior in this acidity region is cation exchange. The data suggest that indium exists predominantly as $InCl_2^+$ cation in aqueous phase under these conditions and was exchanged with [$Hbet^+$] cation in organic phase.

In addition, it should be noted that our models do not consider the presence of water molecules in the metal coordination sphere, which is known to occur. [49, 61]

The analysis of Tl(III) extraction data in the absence and presence of betaine shows three distinct regions in each system (Fig. 9). As can be seen, the general trend is the same, indicating that additional betaine does not affect the speciation of the extracted complexes. The estimated values of extraction constants according to the models discussed above are presented in Tables 5 – 7.

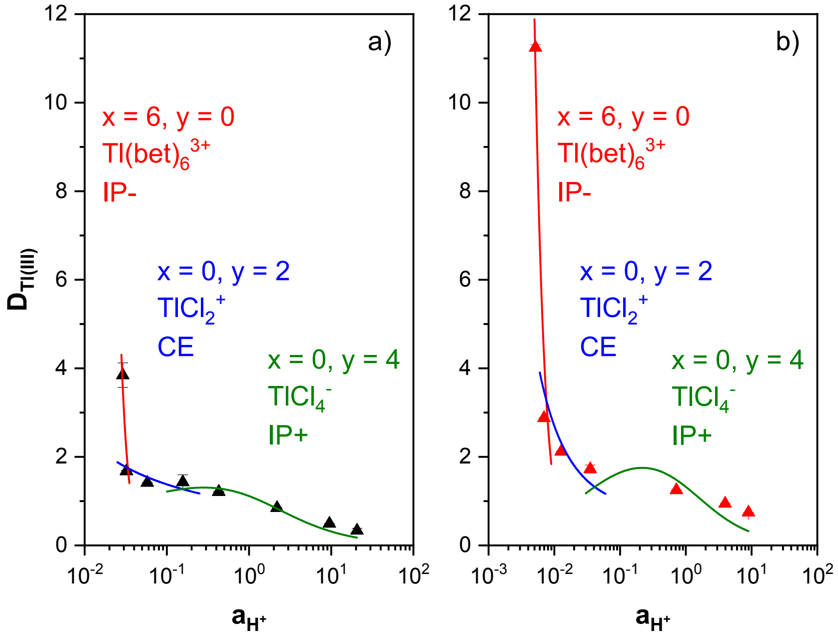

Fig. 9. The plot of $D_{Tl(III)}$ versus a_{H^+} in the absence **(a)** and presence of 15% (w/v) betaine **(b)**. Thallium was oxidized using chlorine water. The lines are results of fitting according to equations in sections 3.5.1 – 3.5.4.

In Table 5, the calculated $K_{ext\ Tl(III)} \cdot K_{Tl(III)}$ values for two possible extraction mechanisms based on ion pair formation with negatively charged organic counter ion and cation exchange in a dilute acid region (Fig. 9, red curve) are presented. The best fit was found for *x* = 6 and *y* = 0. The calculated values suggest that the former mechanism dominates in the considered region because the ion pair formation constant products are four orders of magnitude greater than those of cation exchange. Thus, the extracted species is $[Tl(bet)_6][Tf_2N]_3$.

Table 5. Estimated values of $K_{ext\_IP^-\ Tl(III)} \cdot K_{Tl(III)}$ for ion pair formation and cation exchange mechanisms at low acidity (*x* = 6 and *y* = 0).

	Tl(bet)$_6^{3+}$	
Mechanism	**Absence of betaine**	**15% (w/v) betaine**

$\mathrm{K_{ext\_IP^-\ Tl(III)}} \cdot \mathrm{K_{Tl(III)}}$	(4.6 ± 0.6)·10^{-4}	(1.27 ± 0.15)·10^{-7}
$\mathrm{K_{ext\_CE\ Tl(III)}} \cdot \mathrm{K_{Tl(III)}}$	(4.9 ± 0.6)·10^{-8}	(1.15 ± 0.09)·10^{-11}

The $\mathrm{K_{ext\ Tl(III)}}$ values are reported in Table 6. According to a Tl(III) speciation study, [46] Tl(III) predominantly exits as $TlCl_2^+$ species in this acid range (Fig. 9, blue curve). Also, our data in Fig. 4 show that Tl(III) extraction in this acidity region does not depend on $[Tf_2N^-]$ anion concentration. Thus, on the basis of thallium speciation in the aqueous chloride solution and its behavior in the presence of $Li[Tf_2N]$ salt, the cation exchange mechanism is the only possible extraction route. The best fit was found for $x = 0$, which means no betaine is involved in the formation of the extracted complex, and $y = 2$.

Table 6. Estimated values of $\mathrm{K_{ext\ Tl(III)}}$ according to the cation exchange mechanism ($x = 0$ and $y = 2$).

$TlCl_2^+$		
Mechanism	**Absence of betaine**	**15% (w/v) betaine**
$\mathrm{K_{ext\_CE\ Tl(III)}}$	0.465 ± 0.024	1.16 ± 0.16

It is known that $TlCl_4^-$ species is predominant at high acid concentration ($a_{\mathrm{H^+}} > 0.2$) [46] and this species is extracted by ionic liquids. [41, 47] However, formation of a non-extractable $TlCl_5^{2-}$ complex was also reported. [52, 62] In our previous paper we found an equation to describe Tl(III) extraction from the same HCl media into another ionic liquid. [63] By analogy the equation that reflects simultaneous presence of two thallium species with one of them extracted into [Hbet][Tf_2N] can be written:

$$\mathrm{D_{IP^+\ TlCl_4^-}} = \frac{\mathrm{K_{ext\_IP^+\ TlCl_4^-}} \cdot [\mathrm{Hbet^+}]_{\mathrm{aq}}}{1 + \mathrm{K_5} \cdot a_{\mathrm{H^+}}} \qquad \text{Eq. 31}$$

where K_5 is a stepwise stability constant to form $TlCl_5^{2-}$ from $TlCl_4^-$. Based on literature data, the average value of this constant is 0.68. [52, 62] This leads to the conclusion that the $TlCl_4^-$ species was extracted through ion pair formation with [$Hbet^+$] cation and corresponding calculations are presented in Table 7.

Table 7. Estimated values of $\mathrm{K_{ext\_IP^+\ TlCl_4^-}}$ for ion pair formation mechanism ($x = 0$ and $y = 4$).

$TlCl_4^-$

Mechanism	**Absence of betaine**	**15% (w/v) betaine**
$K_{ext\_IP^+\ TlCl_4^-}$	3.84 ± 0.35	1.54 ± 0.39

Distribution ratios of Tl(I) versus hydrogen ion activity are plotted in Fig. 10. Again, three distinct regions can be found in the plots. In the entire acid region, the addition of betaine does not seem to have a significant impact on the extracted complex.

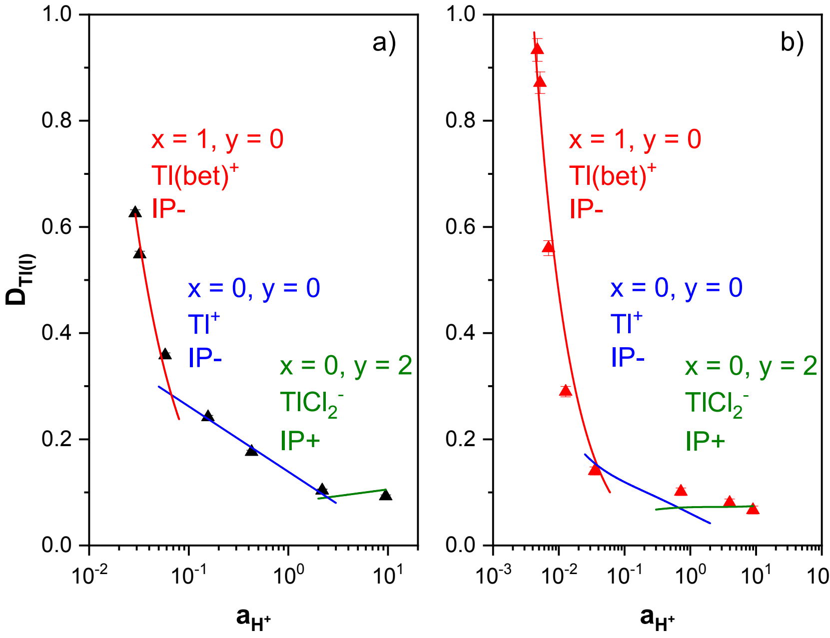

Fig. 10. The plot of $D_{Tl(I)}$ versus a_{H^+} in the absence **(a)** and presence of 15% (w/v) betaine **(b)**. The lines are results of fitting according to equations in sections 3.5.1 – 3.5.4.

Based on the study of Tl(I) speciation, both Tl^+ and $TlCl_2^-$ are likely to exist in HCl media.[64] As a comparison, Table 8 shows the calculated $K_{ext\ Tl(I)} \cdot K_{Tl(I)}$ values for the low acidity range. The best fit was found for *x* = 1 and *y* = 0. Based on the optimal fit, the ion pair formation mechanism between Tl(bet)$^+$ and [Tf_2N^-] is a predominant path because the cation exchange values are one order of magnitude less. Thus, extracted species is [Tl(bet)][Tf_2N].

Table 8. Estimated values of $K_{ext\ Tl(I)} \cdot K_{Tl(I)}$ for ion pair formation and cation exchange mechanisms at low acidity (*x* = 1 and *y* = 0).

$Tl(bet)^+$		
Mechanism	**Absence of betaine**	**15% (w/v) betaine**
$K_{ext\_IP^-\ Tl(I)} \cdot K_{Tl(I)}$	0.280 ± 0.008	(1.83 ± 0.07)·10^{-2}
$K_{ext\_CE\ Tl(I)} \cdot K_{Tl(I)}$	0.069 ± 0.004	(4.31 ± 0.16)·10^{-3}

It has been seen above that increase of HCl acid concentration leads to removal of betaine from the metal coordination sphere. This is the reason why the trend of $D_{Tl(I)}$ values is changed upon increase of acidity. Table 9 shows result of fitting for the next acidity range (Fig. 10, blue curve). The best fit was found for *x* = 0 and *y* = 0. According to calculated values, the ion pair formation between Tl^+ and $[Tf_2N^-]$ is the main route for the metal extraction in this acidity range.

Table 9. Estimated values of $K_{ext\ Tl(I)}$ according to the ion pair formation mechanism (*x* = 0 and *y* = 0).

Tl^+		
Mechanism	**Absence of betaine**	**15% (w/v) betaine**
$K_{ext\_IP^-\ Tl(I)}$	1.302 ± 0.031	1.55 ± 0.32

The very last segment in Fig. 10 is attributed to the extraction of $TlCl_2^-$, which is the predominant anionic Tl(I) species in this acid region. [64] This negatively charged species explains the $D_{Tl(I)}$ trend change with increasing HCl concentration (conditions that favor anionic complex formation). This change is in agreement with our previously published data on Tl(I) extraction from HCl media into a set of imidazolium ionic liquids. [47] The best fit was found for *x* = 0 and *y* = 2. Based on the calculated values given in Table 10, the ion pair formation is the predominant mechanism of extraction of $[Hbet][TlCl_2]$.

Table 10. Estimated values of $K_{ext\ Tl(I)}$ for ion pair formation mechanisms

$TlCl_2^-$

Mechanism	Absence of betaine	15% (w/v) betaine
$K_{ext\_IP^+ Tl(I)}$	0.166 ± 0.023	0.050 ± 0.005

4. Conclusion

In all systems that were studied, it was found that In and Tl(III) were extracted into water-saturated [Hbet][Tf_2N] ionic liquid and the highest distribution ratios were 200 and 70, respectively, at low HCl concentrations in the presence of 15% (w/v) betaine. The study on extraction kinetics for both metals showed that the equilibrium was attained within 1 min. The presence of the mineral acid played an important role as it controlled the aqueous solubility of the ionic liquid, the dissociation of [$Hbet^+$], the protonation of [Tf_2N^-] and the speciation of the metal complexes. Increasing hydrochloric acid concentration decreased the distribution ratios of all metals due to changes in their speciation, having the highest impact on indium, while the effect on Tl(III) and Tl(I) transfer was less significant.

Addition of zwitterionic betaine into the chemical system promoted the solubility of [Hbet][Tf_2N] in the aqueous phase. As the result, the distribution ratios of both In and Tl(III) increased by almost one order of magnitude, especially at low HCl concentrations. A study of In and Tl(III) extraction dependency on Li[Tf_2N] concentration was also performed to confirm the role of the ionic liquid anion in the transfer of the metals. The results showed that the increased amount of [Tf_2N^-] led to higher indium distribution ratios but it had no effect on Tl(III) behavior. This suggests that this anion is responsible for In extraction and does not involved in Tl(III) transfer.

Several mathematical models were developed to explain the extraction mechanisms of In, Tl(III) and Tl(I) into [Hbet][Tf_2N]. These models considered extraction through ion pair formation with either [Tf_2N^-] or [$Hbet^+$] in the aqueous phase, cation exchange with [$Hbet^+$] and anion exchange with [Tf_2N^-] in the organic phase. All of the proposed theoretical mechanisms are based on the initial interaction of metals and their halide complexes with [$Hbet^+$] in the aqueous phase, leading to betaine-containing complexes. Then, the extraction data were fitted according to the models proposed to determine the number of betaine ligands extracted with the metal ion, and ultimately, the structure of the extracted complex. These models also allowed for estimating of the extraction constants of the products transferred between phases and the constants of complexes formed in the aqueous phase ($K_{ext\,M(III),\ Tl(I)} \cdot K_{M(III),\ Tl(I)}$). The results of the mathematical treatment combined with the expected chemical behavior of the metals show that all metals contain betaine in their coordination sphere at a very low HCl concentration, resulting in the $In(bet)_6^{3+}$, $Tl(bet)_6^{3+}$, and $Tl(bet)^+$ corresponding complexes extraction through the ion pair formation mechanism with [Tf_2N^-] anion. At higher HCl concentrations, regardless of the presence or absence of additional betaine in the aqueous phase, we suggest that In and Tl(III) are predominantly extracted as positively charged dichlorocomplexes ($InCl_2^+$ and $TlCl_2^+$) via cation exchange mechanism with [$Hbet^+$] cation in the organic phase. Meanwhile, Tl(I) was extracted in this acidity region according to the ion pair formation between Tl^+ and [Tf_2N^-]. Extraction of negatively charged complexes was found only for thallium. The dominant extraction mechanism for Tl(III) in > 0.2 M HCl is ion pair formation of $TlCl_4^-$ with [$Hbet^+$], despite the presence of non-extractable $TlCl_5^{2-}$ in the aqueous phase. And monovalent thallium forms $TlCl_2^-$ species in > 5 M HCl, which then is extracted as [Hbet][$TlCl_2$] according to the ion pair formation mechanism. The presence of 15% (w/v) betaine did not affect the metals speciation according to our analysis.

Conflicts of interest

There are no conflicts of interest to declare.

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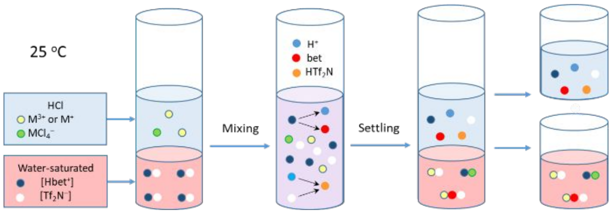

Carrier-free In and Tl were extracted into a protic ionic liquid [Hbet][Tf_2N] from HCl media with and without the presence of zwitterionic betaine in the aqueous phase.